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Title of invention: Catalytic converter apparatus

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SPECIFICATION

1. Title of invention

Catalytic converter apparatus

2. Scope of claims

(1) Catalytic converter apparatus characterised as apparatus accommodating a plurality of exhaust gas cleaning catalysts within a single catalytic converter, wherein the catalyst (A) on the exhaust gas inlet side comprises (a) rhodium and platinum or (b) rhodium, platinum and palladium while the catalyst (B) on the exhaust outlet side comprises palladium and rhodium, and wherein the volume ratio {(A):(B)} of the catalyst (A) on the exhaust gas inlet side to the catalyst (B) on the exhaust outlet side is between 8:1 and 1:3.

3. Detailed description of invention

[Field of industrial utility]

The invention relates to catalytic converter apparatus for automotive exhaust gas clean-up.

[Prior art]

The catalysts used for automotive exhaust gas clean-up are usually three-way catalysts simultaneously removing hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) (a property hereunder referred to as 3-way performance).

The recent trend towards fuel-economy engines of higher power has generated a pressing need for catalysts of outstanding cleaning performance. Moreover, much tougher exhaust gas controls than hitherto are being introduced, especially for HC. Seen in this context, existing catalysts can hardly be considered adequate in 3-way performance.

Although motor vehicles are normally operated in the vicinity of the theoretical air/fuel ratio, a problem arises in that a fuel rich atmosphere develops during acceleration (hereunder referred to as operation "at rich A/F" or "under fuel rich conditions") with the result that a large amount of HC is discharged. The HC cleaning performance must accordingly be enhanced at rich A/F.

Catalytic converter apparatus has been disclosed (Japan Patent Kokai No.55-164715) wherein, as a catalyst effecting more complete combustion of HC and CO, an oxidation catalyst is provided on the inlet side and a reduction catalyst is provided on the outlet side, and wherein the catalyst on the outlet side is divided into platinum (Pt) at the front and rhodium (Rh) at the rear; however, the present invention belongs in a different category since the former apparatus uses rhodium in the catalyst on the converter outlet side only (not on the inlet side), and has a diffusion chamber between the catalysts on the inlet and outlet sides.

Also previously disclosed as apparatus dividing the catalyst between the inlet and outlet sides is a catalytic converter (Japan Patent Kokai No.49-41772) wherein a high temperature activity catalyst (titanium, chromium, etc) is supported upstream and a low temperature activity catalyst (noble metal) is supported downstream; and a catalytic converter (Japan Patent Kokai No.64-7935) wherein the washcoat loading, noble metal loading, cerium content and cell density for a three-way catalyst are separately specified for catalysts on the inlet and outlet sides. However, specific information on the catalysts is scant and further investigation would be needed before the said inventions could be practised. Although a catalytic converter using a plurality

of catalysts of different heat capacity has been disclosed (Japan Utility Model Kokai No.56-50716), no specific values are given and since the aim is simply to provide a small catalyst for start-up, the converter lacks a capacity for combustion of HC and CO.

[Problem addressed by invention]

What is needed now that much tougher exhaust gas controls than hitherto are being introduced is an inexpensive catalytic converter with a high performance in cleaning the exhaust gas of high HC content discharged in a fuel rich environment.

[Means of solving the problem]

The solution is (1) catalytic converter apparatus characterised as apparatus accommodating a plurality of exhaust gas cleaning catalysts within a single catalytic converter, wherein the catalyst (A) on the exhaust gas inlet side comprises (a) rhodium and platinum or (b) rhodium, platinum and palladium while the catalyst (B) on the exhaust outlet side comprises palladium and rhodium, and wherein the volume ratio {(A):(B)} of the catalyst (A) on the exhaust gas inlet side to the catalyst (B) on the exhaust outlet side is between 8:1 and 1:3.

The inventors have found that, in terms of capacity for HC oxidation, palladium (Pd) affords outstanding clean-up of unsaturated HC while platinum (Pt) affords outstanding clean-up of saturated HC. By combining catalysts as above to maximise the expression of these properties, it was possible to enhance clean-up capacity under fuel rich conditions, especially HC clean-up, when the catalyst volume ratio on the exhaust gas inlet and outlet sides was in the range 8:1 to 1:3.

Another benefit of the invention is that, compared with the conventional arrangement whereby a single catalyst containing platinum and rhodium is accommodated in the catalytic converter, palladium can be substituted for platinum on the outlet side. Since palladium is less expensive than platinum, this has the effect of reducing costs. Moreover, the aforesaid performance enhancement is also obtained with a tri-metal (Pt, Pd, Rh) catalyst whereby part of the platinum in the exhaust inlet side catalyst is replaced with palladium, further reducing costs.

The volume ratio of the catalyst on the exhaust gas inlet side to the catalyst on the exhaust gas outlet side is between 8:1 and 1:3.

A volume on the inlet side below the aforesaid 1:3 volume ratio leads to a decline in NO_x clean-up while a volume on the inlet side above the aforesaid 8:1 volume ratio diminishes the enhancement in HC clean-up at rich A/F.

The aforesaid palladium, rhodium or platinum are supported on metal oxides, examples whereof may be listed as activated alumina, α-alumina, silica, titania, silica-

alumina, iron oxide, nickel oxide, alkali metal oxides, alkaline earth metal oxides and rare earth metal oxides.

In addition, cerium oxide (hereunder called "ceria") is contained in at least the exhaust inlet side catalyst, and is preferably contained in both the exhaust inlet side and outlet side catalysts.

[Working examples]

The invention is described in further detail hereunder with working examples; obviously, the invention is not limited to the examples so long as its essential content is adhered to.

Working Example 1

An aqueous nitric acid solution of dinitrodiammineplatinum (Pt content 100 g/l) 41.7 ml and aqueous rhodium nitrate solution (Rh content 50 g/l) 16.7 ml were diluted to 500 ml with pure water, and activated alumina 500 g was introduced into the solution; after mixing, the material was dried for 3 hours at 150°C and calcined for 2 hours at 400°C to obtain platinum- and rhodium-supporting alumina. A slurry was then obtained by wet-pulverising 500 g of the platinum- and rhodium-supporting alumina with 250 g of ceria. The same monolithic support as above, 0.85 l, was immersed in the slurry, excess slurry was blown off, and the support was dried for 3 hours at 150°C; the completed catalyst for the inlet side was then obtained by calcining for 2 hours at 400°C. *[see Amendment (1)]*

The catalyst thus obtained supported platinum and rhodium at Pt 0.83 g and Rh 0.17 g per litre (the weight per litre of catalyst will hereunder be represented as "g/l").

Aqueous palladium nitrate solution (Pd content 100 g/l) 41.7 ml and aqueous rhodium nitrate solution (Rh content 50 g/litre) 16.7 ml were diluted to 500 ml with pure water, and activated alumina 500 g was introduced into the solution; after mixing, the material was dried for 3 hours at 150°C and calcined for 2 hours at 400°C to obtain palladium- and rhodium-supporting alumina.

A slurry was then obtained by wet-pulverising 500 g of the palladium- and rhodium-supporting alumina with 250 g of ceria.

Monolithic support 0.85 l was immersed in the slurry, excess slurry was blown off, and the support was dried for 3 hours at 150°C; the completed catalyst for the outlet side was then obtained by calcining for 2 hours at 400°C. *[see Amendment (2)]*

The catalyst thus obtained supported Pd 0.83 g/l and Rh 0.17 g/l.

Working Example 2

A catalyst was obtained as in Working Example 1 except that the platinum and rhodium of the exhaust inlet side catalyst were substituted with platinum, palladium and rhodium at respectively 0.42 g/l, 0.42 g/l and 0.17 g/l.

Working Examples 3-5

Catalysts were obtained as in Working Example 1 except that the catalyst volumes on the exhaust inlet side and outlet side were varied. The results are given in Table 1.

Note that the amounts of palladium, rhodium and platinum per litre of catalyst are the same throughout.

Comparative Example 1

Catalysts were obtained as in Working Example 1 except that platinum and rhodium were supported at respectively 0.83 g/l and 0.17 g/l on the exhaust outlet side catalyst instead of the palladium and rhodium in Working Example 1. The exhaust inlet side catalyst was obtained as in Working Example 1.

Comparative Example 2

Catalysts were obtained as in Working Example 1 except that palladium and rhodium were supported at respectively 0.83 g/l and 0.17 g/l on the exhaust inlet side catalyst instead of the platinum and rhodium in Working Example 1. The exhaust outlet side catalyst was obtained as in Working Example 1.

Comparative Examples 3 and 4

Catalysts were obtained as in Working Example 1 except that the volumes of the exhaust inlet side and outlet side catalysts in Working Example 1 were varied. The results are given in Table 1. The amounts of palladium, rhodium and platinum per litre of catalyst are the same as in Working Example 1.

Working Example 6

Catalyst performance in HC, CO and NO clean-up under high temperature conditions at rich air/fuel ratios after engine endurance running was examined for the catalysts of Working Examples 1-5 and Comparative Examples 1-4.

(Endurance conditions)

The endurance run used a commercial electronically controlled engine and was conducted with different catalytic converters fitted. The inlet temperature was 850°C and the engine was run for 100 hr.

(Performance under fuel rich conditions at high temperature)

Catalyst performance under fuel rich conditions at high temperature was then studied under the following conditions with the catalyst intake temperature at 400°C. The air/fuel ratio (or A/F) of the engine was varied continuously between 15 and 14 (a sinusoidal signal of 1 Hz was applied to the engine control block from an external oscillator to effect ±1.0 A/F oscillation of frequency 1 Hz in the air/fuel ratio). The Table 2 shows the clean-up (Conv.) under the fuel rich A/F of 14.4.

From Table 2, the catalysts of Working Examples 1-5 of the invention are remarkably more effective than the Comparative Examples 1-3 in clean-up under fuel rich conditions at high temperature, especially in the clean-up of HC; moreover the aforesaid catalytic performance is further enhanced within the range of volume ratio of the exhaust gas inlet and outlet side catalysts in the invention, and as the aforesaid high performance is exhibited notwithstanding the substitution of expensive platinum with less expensive palladium, a reduction in costs can be secured.

Table 1

Catalyst	Catalyst on exhaust gas inlet side		Catalyst on exhaust gas outlet side		Catalyst volume ratio (inlet/outlet)
	Catalyst composition (g/l)	Volume (l)	Catalyst composition (g/l)	Volume (l)	
Working Example 1	Pt = 0.83 Rh = 0.17	0.85	Pd = 0.83 Rh = 0.17	0.85	1/1
Working Example 2	Pt = 0.42, Pd = 0.42, Rh = 0.17	0.85	Pd = 0.83 Rh = 0.17	0.85	1/1
Working Example 3	Pt = 0.83 Rh = 0.17	1.20	Pd = 0.83 Rh = 0.17	0.50	2.4/1
Working Example 4	Pt = 0.83 Rh = 0.17	1.51	Pd = 0.83 Rh = 0.17	0.19	8/1
Working Example 5	Pt = 0.83 Rh = 0.17	0.42	Pd = 0.83 Rh = 0.17	7.28	1/3
Comparative Example 1	Pt = 0.83 Rh = 0.17	0.85	Pt = 0.83 Rh = 0.17	0.85	1/1
Comparative Example 2	Pd = 0.83 Rh = 0.17	0.85	Pd = 0.83 Rh = 0.17	0.85	1/1
Comparative Example 3	Pt = 0.83 Rh = 0.17	1.545	Pd = 0.83 Rh = 0.17	0.155	9/1
Comparative Example 4	Pt = 0.83 Rh = 0.17	0.28	Pd = 0.83 Rh = 0.17	1.42	1/5

Table 2 Performance at rich A/F after endurance run (A/F = 14.4)

Catalyst	HC Conv. (%)	CO Conv. (%)	NO Conv. (%)
Working Example 1	88	74	99
Working Example 2	88	73	99
Working Example 3	87	72	99
Working Example 4	88	72	99
Working Example 5	87	72	99
Comparative Example 1	74	65	99
Comparative Example 2	80	64	94
Comparative Example 3	83	69	99
Comparative Example 4	84	70	95

Applicant: Japan Catalytic Chemical Industry Co.

Procedural Amendment (Voluntary)

24 October 1989

[Date stamp: Reception Desk, Patent Office Applications Section, 24/10/89]

To: F.Yoshida, Commissioner, Patent Office, Japan.

1. Subject: Patent Application No. H1-230347

2. Title of invention: Catalytic converter apparatus

3. Person making amendment:

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4. Object of amendment: (1) Specification - Detailed description of invention

5. Content of amendment

(1) Original Specification. p.6, last line-p.7, line 1: *[Working Example 1]*

"The same monolithic support as above, 0.85 l, was immersed in the slurry,..." is corrected to

"A monolithic support (cordierite honeycomb monolithic support (manufacturer: NGK Insulators Co., containing approximately 400 open cells per square inch of cross-section) 0.85 l was immersed in the slurry,..."

(2) Original Specification, p.7, line 17: *[Working Example 1]*

"Monolithic support 0.85 l was immersed in the slurry,..." is corrected to

"The same monolithic support as above, 0.85 l, was immersed in the slurry,..."